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Real-time quantitative detection of styrene in atmosphere in presence of other volatile-organic compounds using a portable device

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Corresponding Author:	Luca Malfatti University of Sassari: Universita degli Studi di Sassari ITALY
First Author:	Francesco Radica
Order of Authors:	Francesco Radica Giancarlo Della Ventura Luca Malfatti Mariangela Cestelli Guidi Annalisa D'Arco Antonio Grilli Augusto Marcelli Plinio Innocenzi
Abstract:	<p>Exposure to styrene is a major safety concern in the fibreglass processing industry. This compound is classified by the International Agency for Research on Cancer as a possible human carcinogen. Several analytical equipment types can detect volatile organic compounds (VOCs) in the atmosphere; however, most of them operate ex-situ exclusively or do not provide easy discrimination between different molecules. This work introduces an improved and portable method based on FTIR spectroscopy to analyse toxic gaseous substances in working sites. Styrene and a combination of VOCs typically associated with the same styrene in industrial processes, such as acetone, ethanol, xylene and isopropanol, have been used to calibrate and test this methodology.</p> <p>The results demonstrate that this technique offers the possibility to discriminate between different gaseous compounds in the atmosphere with a high degree of confidence, and allows obtaining very accurate quantitative information on their concentration, down to the ppm level, even when different VOCs are present in a mixture.</p>
Suggested Reviewers:	<p>Gianfelice Cinque Diamond Light Source Ltd gianfelice.cinque@diamond.ac expert in infrared spectroscopy</p> <p>Ulrich Shade Helmholtz Zentrum Berlin: Helmholtz-Zentrum Berlin für Materialien und Energie GmbH ulrich.schade@helmholtz-berlin.de expert in real-time infrared spectroscopy</p> <p>Lisa Vaccari Elettra Sincrotrone Trieste SCpA lisa.vaccari@elettra.eu expert in infrared spectroscopy</p>

Opposed Reviewers:	
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UNIVERSITA' DEGLI STUDI DI SASSARI

chemistry/pharmacy

Dear Editor,

We submit to your kind attention our manuscript entitled "*Real-time quantitative detection of styrene in atmosphere in presence of other volatile-organic compounds using a portable device*" for publication in "*Talanta*".

Real-time analysis of toxic indoor volatile organic compounds is of paramount importance for industrial processing. Exposure to volatile organic compounds can, in fact, be a major safety concern for the workers. Our manuscript describes the use of a detection technique based on infrared spectroscopy. The method relies on a sensitive and fast readout of the organic vapors present in the atmosphere and provides better performances than commercial sensors based on Photo-Ionization Detector (PID). Moreover, our method is capable of discriminating and detect several types of VOCs, such as styrene acetone, ethanol, xylene, and isopropanol without being affected by mutual interference. After validating the sensing technique, we calibrated the method towards the specific detection of styrene, achieving remarkable precision down to ppm concentration level. Finally, we also tested the potential of a commercial FTIR spectrometer to be used as a portable VOCs' detector.

We deeply believe that this work could be of interest to the broad community working in the field of air pollution sensors.

Best regards,
Plinio Innocenzi

Plinio Innocenzi

Full Professor of Materials Science

LMNT Laboratory of Materials Science and Nanotechnology

Department of Chemistry and Pharmacy

Via Vienna 2, - 07100 Sassari (SS)

Tel. lab.: +39 079 998630

Fax: +39 079 9720420

E-mail: plinio@uniss.it

Novelty Statement

We have used FTIR spectroscopy to detect volatile organic compounds (VOCs) in the environment.

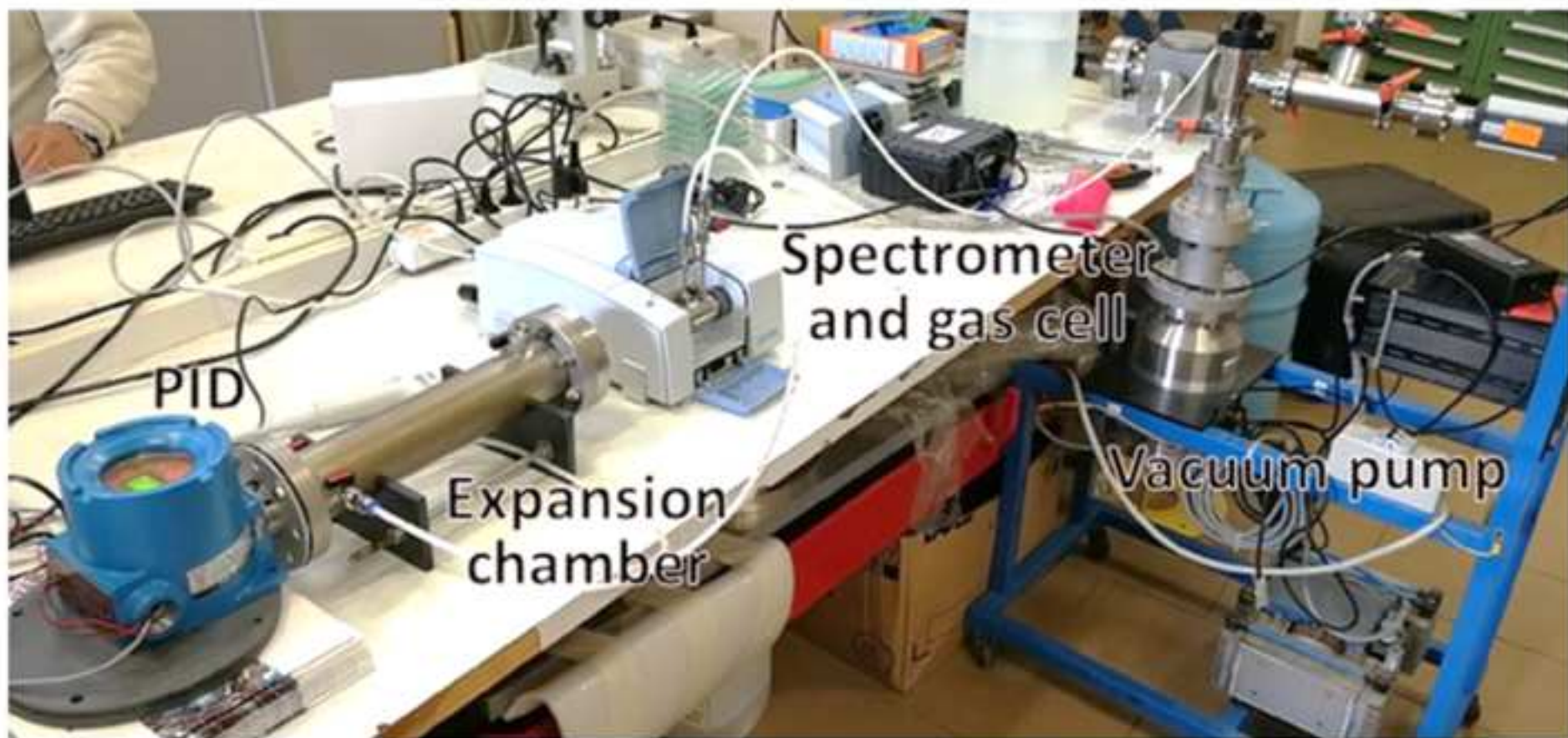
Infrared detection shows a faster response than standard Photo-Ionization-Detection (PID)

Different VOCs can be discriminated efficiently by using the appropriate spectral region where the band overlaps are minimized. This is impossible with PID.

A portable FTIR spectrometer has been successfully used to design of a detection system suitable for work sites that require monitoring of styrene in the atmosphere.

Highlights

- Exposure to VOCs is a serious safety issue for industrial processing
- An FTIR-based sensing method allows for a fast and reliable VOCs' detection down to ppm
- The method easily discriminates acetone, styrene, xylene, isopropanol, and acetone vapors.
- Precise calibration to determine styrene concentration in the atmosphere is achieved.



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**Real-time quantitative detection of styrene in atmosphere in presence
of other volatile-organic compounds using a portable device**

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**Francesco Radica^{1,2}, Giancarlo Della Ventura^{1,2,3}, Luca Malfatti⁴, Mariangela
Cestelli Guidi², Annalisa D'Arco⁵, Antonio Grilli², Augusto Marcelli^{2,6}, Plinio
Innocenzi^{4§}**

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¹ Department of Science, Università Roma Tre, viale Guglielmo Marconi 446, 00146,
Roma, Italy

² Istituto Nazionale di Fisica Nucleare - LNF, Via Enrico Fermi 54, 00044 Frascati,
Italy

³ Istituto Nazionale di Geofisica e Vulcanologia, Via di Vigna Murata 605, 00143
Roma, Italy

⁴ Department of Chemistry and Pharmacy, Laboratory of Materials Science and
Nanotechnology, CR-INSTM, via Vienna 2, 07100, Sassari, Italy

⁵ Istituto Nazionale di Fisica Nucleare - Section of Rome "La Sapienza", P. Aldo Moro
5, 00185 Rome

⁶ Rome International Centre for Materials Science Superstripes, via dei Sabelli 119A,
00185 Rome, Italy

[§] Corresponding author: plinio@uniss.it

1 **Abstract:** Exposure to styrene is a major safety concern in the fibreglass processing
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3 industry. This compound is classified by the International Agency for Research on
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5 Cancer as a possible human carcinogen. Several analytical equipment types can detect
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7 volatile organic compounds (VOCs) in the atmosphere; however, most of them operate
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9 ex-situ exclusively or do not provide easy discrimination between different molecules.
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11 This work introduces an improved and portable method based on FTIR spectroscopy to
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13 analyse toxic gaseous substances in working sites. Styrene and a combination of VOCs
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15 typically associated with the same styrene in industrial processes, such as acetone,
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17 ethanol, xylene and isopropanol, have been used to calibrate and test this methodology.
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19 The results demonstrate that this technique offers the possibility to discriminate between
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21 different gaseous compounds in the atmosphere with a high degree of confidence, and
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23 allows obtaining very accurate quantitative information on their concentration, down to
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25 the ppm level, even when different VOCs are present in a mixture.
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35 **Keywords:** Volatile organic compounds; environmental sensors; infrared spectroscopy
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1 **Introduction**
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3 Volatile organic compounds (VOC) generated as by-products of various
4 industrial activities are among the main environmental concerns in industrialized
5 countries for both outdoor and indoor pollution. Fundamental studies [1] have
6 correlated VOC pollution in urban areas with the intensive use of petrochemical-
7 derived products used in transport and energy production, resulting in photochemical
8 smog and active climate aerosols. On the other hand, very little is known about indoor
9 VOCs pollution, especially in workspaces, and in recent decades they are considered
10 responsible for several casualties [2].
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22 Among the many VOCs, styrene is a colourless substance that evaporates
23 quickly and is mainly linked together as long chains (polystyrene). Styrene poisoning is
24 very dangerous for human health as it attacks the nervous system, leading to changes in
25 colour vision, fatigue, slow response time and problems with concentration. This
26 substance is listed by the WHO International Agency for Research on Cancer as a
27 possible carcinogenic factor in group 2B of Different Occupational Exposure Limits
28 (OELs) [3] which EU members have established. In Italy, for instance, these limits are
29 20 ppm as an 8-hour Time-Weighted-Average (TWA) and 40 ppm as a Short-Term-
30 Exposure-Limit (STEL, 15 min). Compliance with these limits is essential as the
31 industry produces large quantities of styrene, especially during plastics and rubber
32 fabrication. Products containing styrene include packaging materials, fibreglass, plastic
33 pipes, automobile parts, drinking cups and other "food-use" items. As a result, many
34 people are exposed in the workplace to styrene pollution daily, a potentially hazardous
35 condition that requires constant and specific monitoring.
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1 Several types of analytical equipment can detect the different VOCs in the
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3 atmosphere, such as glass-tubes with bleaching media or activated carbon badges
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5 designed for spot visualization of the exposure level, gas sensing semiconductors (GSS)
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7 which have very high sensitivity [4, 5, 6], up to portable analytical instruments based on
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9 Photo-Ionization-Detection (PID) systems, which provide rapid response and the ability
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11 to store data.
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15 A substantial limitation of all the techniques mentioned above is that they do not
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17 allow good discrimination among the different VOCs. On the other hand, analytical
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19 techniques such as gas chromatography GC [7], mass spectroscopy MS [8] and Fourier-
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21 transform infrared spectroscopy, FTIR, although they are very promising both for the
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23 detection of minimum VOC concentrations and able to discriminate among the different
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25 molecular species, they are typical laboratory-based techniques. They are not designed
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27 for in-situ measurements or real-time monitoring and require expensive equipment and
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29 skilled operators. Among these techniques, FTIR has shown to be much more time-
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31 efficient, enabling the design of procedures for higher and more realistic industrial-scale
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33 concentrations [9].
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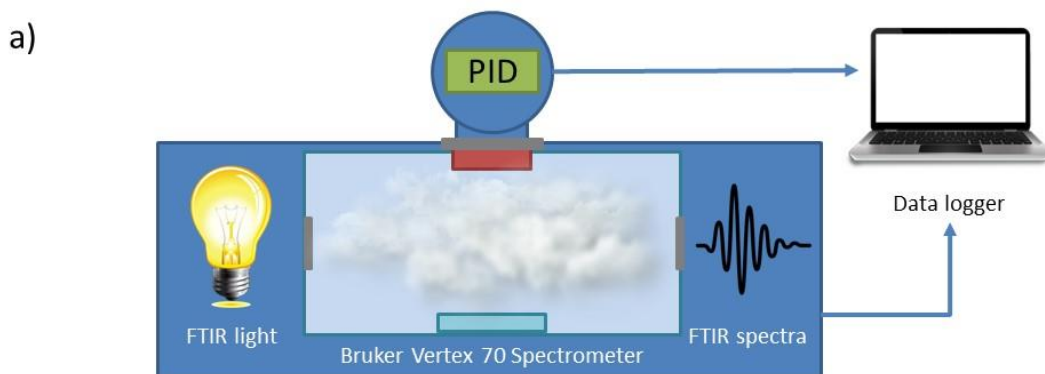
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37 The ability of FTIR spectroscopy to analyse ambient air continuously and in real-time is
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39 an interesting question, mainly due to the ease of the method and the possibility to make
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41 it portable. FTIR in the mid-infrared range (MIR) has very high sensitivities for
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43 ambient-level detection (typically in the ppb range) of common hazardous air pollutants
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45 which are typically strong IR absorbers [10].
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49 The present work aimed to introduce an improved and portable method based on FTIR
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51 spectroscopy to analyse toxic gaseous substances at work sites. Therefore all the
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53 experiments presented and discussed in this article focus on styrene and a combination
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1 of VOCs typically associated with styrene in industrial processes, such as ethanol,
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3 acetone, toluene, xylene and isopropanol. A laboratory FTIR spectrometer coupled to a
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5 photo-ionization detector for simultaneous measurements and calibration has been used
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8 to set up the procedure. Once the correct working conditions were defined, the
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10 transferability and scalability were verified using a portable FTIR spectrophotometer.
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12 This a necessary step for the final design of a new compact device for in situ monitoring
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14 of VOCs in real-time at the working sites.
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21 **Materials and Methods**

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23 Fourier-transform infrared (FTIR) measurements were performed using a Bruker Vertex
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25 70 interferometer. The spectrometer was coupled with a commercial Photo-Ionization
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27 Detector (PID) (TA-2100 Styrene Detector from Mil-Ram Technology, Inc., www.mil-
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46 ram.com) calibrated for the detection of styrene in the range 0-100 ppm. According to
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48 the manufacturer, this sensor has an accuracy of 1 ppm in an interference-free
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50 atmosphere. A schematic drawing of the experimental set-up is shown in **Figure 1**.
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53 **Figure 1.** Schematic view of the benchtop set-up used for the calibration experiments.
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1 The PID system was connected to an external computer for data collection and analysis.
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3 Selected amounts of liquid VOCs were placed on a Corning® Petri dish located inside
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5 the sample chamber (volume ~ 13 L and IR light path length 25.5 cm) and allowed to
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7 evaporate completely. The gas concentration in the chamber was monitored
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9 simultaneously with the PID, every 1 s, and collecting FTIR spectra in continuous
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11 mode, every 30 s for the first hour and then every 60 s. Each experiment lasted from 1
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13 to 3 hours. FTIR spectra were collected averaging 32 scans, with a nominal resolution
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15 of 4 cm⁻¹ in the 5000-400 cm⁻¹ range. One of the primary objectives of this work was a
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17 laboratory calibration for the quantitative determination of styrene in air using FTIR
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19 methods. . We therefore selected a number of common interfering VOCs associated
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21 with styrene in workplaces to be tested alone or simultaneously present with different
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23 amounts of styrene. Detection of interfering VOCs was performed using the same PID
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25 optimized for styrene. Therefore the measured values (i.e. ppmeq) were converted into
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27 the actual concentrations of these gases using appropriate correction factors (CF from
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29 [11]) for a UV lamp at 10.6 eV. A total of 29 experiments were performed with this set-
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31 up for the different VOCs (**Table 1**).

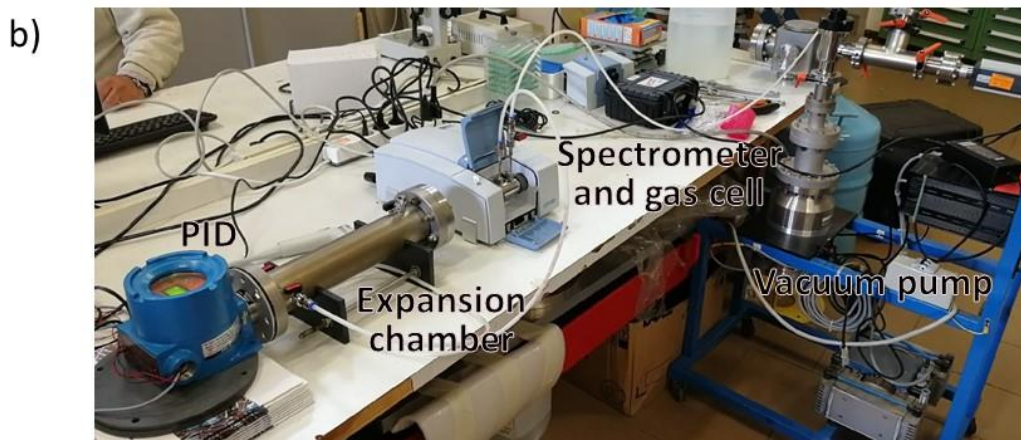
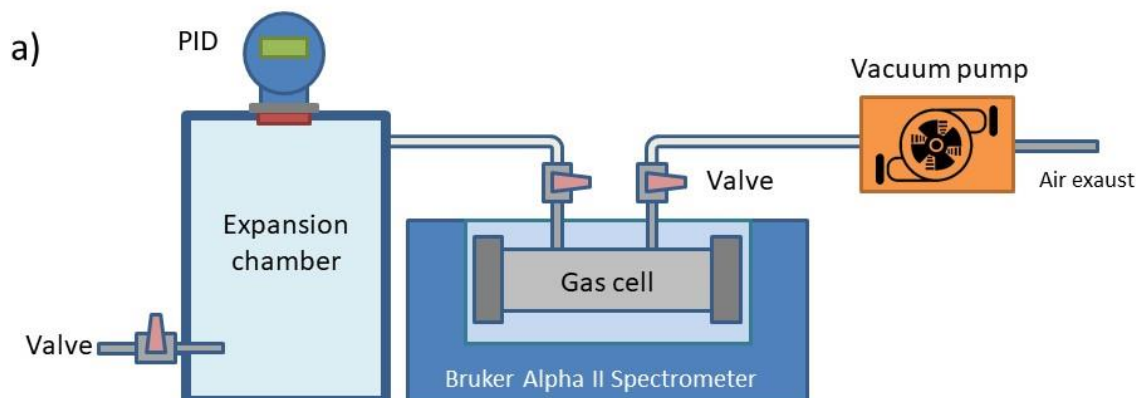
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42 **Table 1.** VOC analysed on benchtop experiments and the amounts of liquid released for
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44 each calibration run inside the spectrophotometer chamber.
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VOC	Dosage / μL
Styrene	1, 2, 3, 4, 5, 6, 8, 10
Toluene	2, 4, 8
Toluene + Styrene	2+2

Acetone	2, 4, 8
Acetone + Styrene	2+2
Ethylene	2, 4, 8
Ethylene + Styrene	2+2
Isopropanol	2, 4, 8
Isopropanol + Styrene	2+2
Xylene (mix meta + orto + para)	2, 4, 8
Xylene + Stirene	2+2

For the calibration of the portable device, we used a Bruker Alpha II spectrometer equipped with a gas cell with a path of 7 cm (cell volume ~ 0.01 L). The gas cell was connected to a sealed evaporation chamber, where the PID sensor was also installed for real-time monitoring of evaporated VOC. **Figure 2** shows a schematic layout of this configuration. For these experiments, different amounts of liquid ethanol, acetone and

1 isopropanol were introduced with a pipette inside the evaporation chamber (chamber
2 volume ~ 1 L), and the concentration monitored against time using the PID sensor. As
3
4 volume ~ 1 L), and the concentration monitored against time using the PID sensor. As
5
6 soon as the PID readings indicated complete evaporation of the liquid within the
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8 chamber, the gas was transferred into the gas cell of the spectrometer. The flow was
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10 ensured by the pre-evacuation of the cell (vacuum pressure around 50 mbar) closed by
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12 two 5 mm thick KBr windows, using a vacuum pump (**Figure 2**). A total of 49
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14 experiments were performed with this setup. Spectra were collected averaging 16 scans,
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16 with a nominal resolution of 4 cm⁻¹ in the 4500-500 cm⁻¹ range, at the scan velocity of
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18 7.5 kHz. Peak integration was performed using embedded OPUS™ 7.0 software using a
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20 linear baseline; data were analysed by the ORIGIN PRO™ software.
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1 **Figure 2.** Laboratory setup used for the calibration experiments on the portable system.

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3 Schematics (a) and picture (b) of the of the setup components.
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10 **Results and discussions**

11 *Curve calibrations for styrene and individual interfering VOCs*

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13 For the first set of experiments performed with the benchtop spectrometer, compounds
14 were introduced into the sample compartment. Different amounts of liquids were
15 deposited via a micropipette on a Petri dish inside the chamber which was immediately
16 closed; the liquid was allowed to evaporate by simultaneously and continuously
17 collecting FTIR spectra and PID readings. **Figure 3a** shows the selected spectra
18 measured in the MID-IR for the different compounds measured. The spectra are
19 identical to those reported in the literature for the same compounds [12]. Note that the
20 strong absorption in the range 2200-2500 cm^{-1} occasionally detected in the spectra (see
21 isopropanol or styrene) is due to atmospheric CO_2 . For the purpose of this work, only
22 two spectral ranges of the MIR region were thoroughly analysed, one centred around
23 900 cm^{-1} and the other at 3100 cm^{-1} , as highlighted by the two red boxes in **Figure 3a**.
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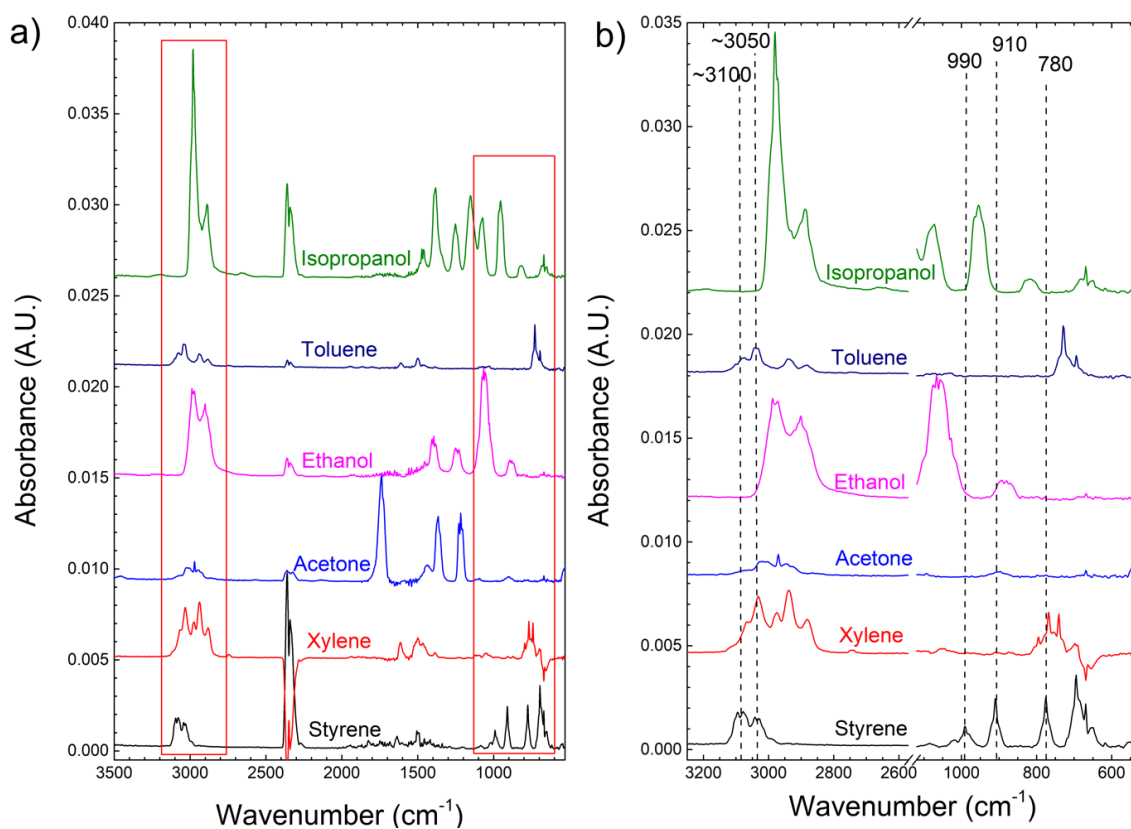
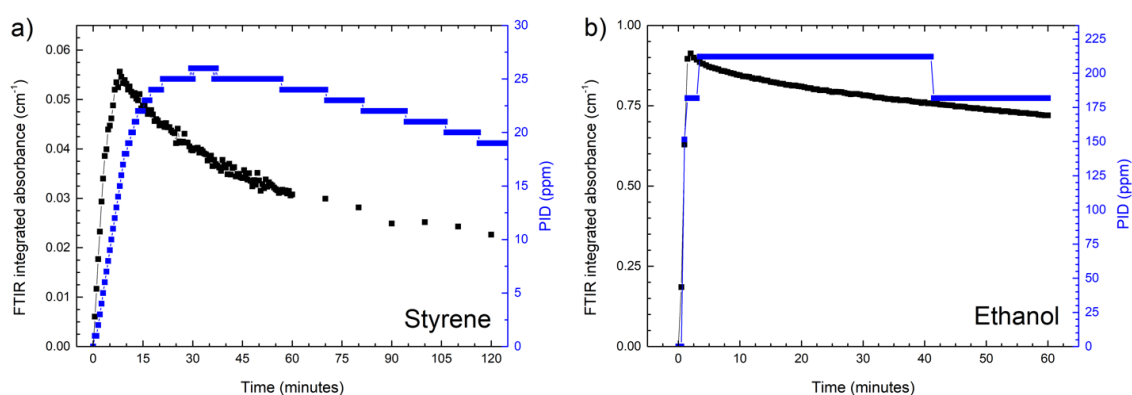


Figure 3. (a) FTIR spectra of selected VOCs in the mid infrared range; the wavenumber ranges in the boxes in Figure (a) are enlarged in Figure (b). The dashed segments show the position of the absorption band peaks (or groups peaks) of interest for styrene.

1 Since the maxima of the absorption band in these wavenumber ranges will be used to
2 evaluate the styrene concentration in the atmosphere, the region of interest has been
3 enlarged in **Figure 3b**; the positions of the styrene bands selected for the analyses are
4 indicated with dashed lines. The infrared spectra in **Figure 3b** show that, although a
5 partial overlap of some bands may occur, the spectra allow the identification of the
6 different VOCs with a high degree of confidence.
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33 **Figure 4.** Typical FTIR integrated absorbance trends (in black) and PID readings (in
34 blue) over time for styrene (a) and ethanol (b). Integrated absorbances (A_i) were
35 obtained by integrating the 910 cm^{-1} styrene band and the 1066 cm^{-1} ethanol absorption
36 bands.
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46 **Figure 4a** shows the results obtained by introducing 2 mL of styrene into the
47 spectrometer chamber. The integrated absorbance (A_i) of the 910 cm^{-1} band (black line)
48 shows a rapid increase in the first minutes and then, once the maximum is reached, there
49 is a slow and continuous decrease. Similarly, a sharp increase in PID readings (blue
50 line) followed by a slow decrease of the signal is observed. While the increase is related
51 to the evaporation of the liquid inside the spectrophotometer chamber, the decrease can
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1 be explained by gas leakage because for a long duration of the experiment (hours) the
2 bench chamber is not perfectly sealed. Furthermore, **Figure 4a** shows that the maxima
3 detected by FTIR and PID do not coincide. The maximum by infrared spectroscopy is
4 observed after 5 minutes while the PID response reaches the maximum 10 minutes
5 after. Finally, the rate of signal decrease is steeper for FTIR than for PID. Similar trends
6 in the FTIR response compared to PID detectors occur in all tests and can vary in
7 intensity according to the different VOC present in the chamber and according to the
8 initial quantity of liquid. In comparison, **Figure 4b** shows the FTIR vs PID response for
9 the experiment with 8 mL of ethanol where for both detectors, the maximum is reached
10 almost simultaneously within the first 5 minutes. The different response observed for
11 the two analytical techniques is associated with different factors, such as different
12 detection systems, response time etc. However, for this configuration we must at least
13 consider that: 1) the PID sensor is positioned above the sample chamber and in a higher
14 position than the FTIR beam path (**Fig. 1a**); therefore, VOCs with higher vapour
15 pressure, such as ethanol, reach the PID detector faster, reducing the interval between
16 the PID and FTIR response; 2) unlike the FTIR detector, in the PID system the gas
17 enters a small ionization chamber where it is photoionized and counted. The gas itself is
18 not immediately cleared from the ionization chamber closed with a permeable
19 membrane that allows the gas flow from outside to the detector and vice-versa. During
20 FTIR measurements, the infrared beam interacts with the gas inside the sample
21 compartment and then reaches the detector where it is counted in real-time. These
22 different layouts are responsible for the different decrease in intensity between the two
23 detection systems.

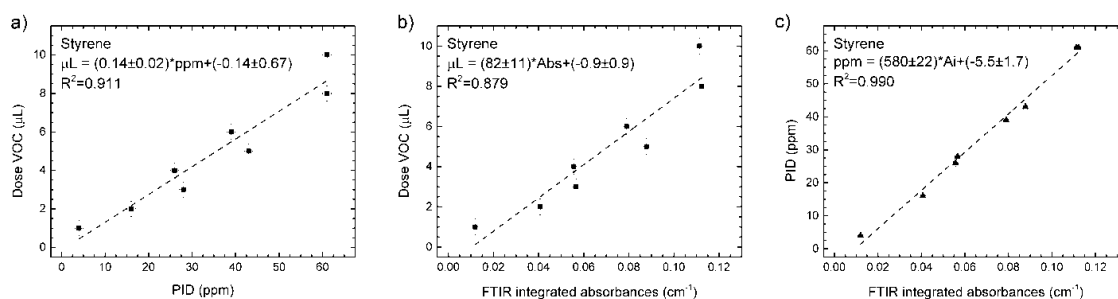


Figure 5. Styrene calibration curves: Dose vs PID (a), Dose vs. FTIR, (b) and PID vs FTIR (c). Integrated absorbances (A_i) of the 910 cm^{-1} band.

The same experiment has been performed for each compound and different amounts of gas injected into the spectrophotometer chamber (**Table 1**). Using dual graphs (integrated IR absorbance and PID reading, **Figure 4**) we have extracted the actual amount (in ppm) of the gas in the atmosphere from the PID reading, and the infrared absorbance of styrene for the different concentrations. **Figure 5a** shows the relationship between the amount (in μL) of liquid placed into the sample chamber versus the PID reading, while **Figure 5b** shows the relationship between the absorbance of the 910 cm^{-1} styrene band in the infrared spectrum. The uncertainty on the integrated absorbances is very low and has been estimated at 0.001 cm^{-1} based on the residual background noise after an average of 32 scan. The uncertainty of the PID readings is set to $\pm 1 \text{ ppm}$ according to the manufacturer and the error for the manual dosing using the pipette was estimated to be $\sim 0.4 \mu\text{L}$. A positive and excellent linear relationship among data points is evident ($R^2 = 0.911$ and 0.879). The poor dispersion of the experimental data is mainly due to the difficulty of dosing and handling small quantities of liquid and their transfer inside the spectrometer chamber. The styrene calibration curves in **Figure 5c** show excellent agreement ($R^2 = 0.990$) between the amount of styrene measured by the

PID system and the integrated absorbance of the selected IR absorption band at 910 cm^{-1} .
 1. In transmission infrared spectroscopy, the integrated absorbance measured on a specific band is related to the quantity of the target molecule via the Beer-Lambert relationship (1) [13]:

$$A_i = \epsilon_i l c \quad (1)$$

where A_i is the integrated absorbance (in cm^{-1}), l = the sampled length (in cm), *i.e.* the optical path of the cell, and c = concentration of the molecule (in ppm). ϵ_i ($\text{ppm}^{-1} \text{cm}^{-2}$) is a matrix-specific absorption coefficient that should be calibrated for any substance. For styrene, the slope resulting from **Figure 5c** was normalized to the path length ($l = 25.5 \text{ cm}$) and the resulting absorption coefficient ϵ_i ($\text{ppm}^{-1} \text{cm}^{-2}$) for the 910 cm^{-1} band is 14800 ± 760 .

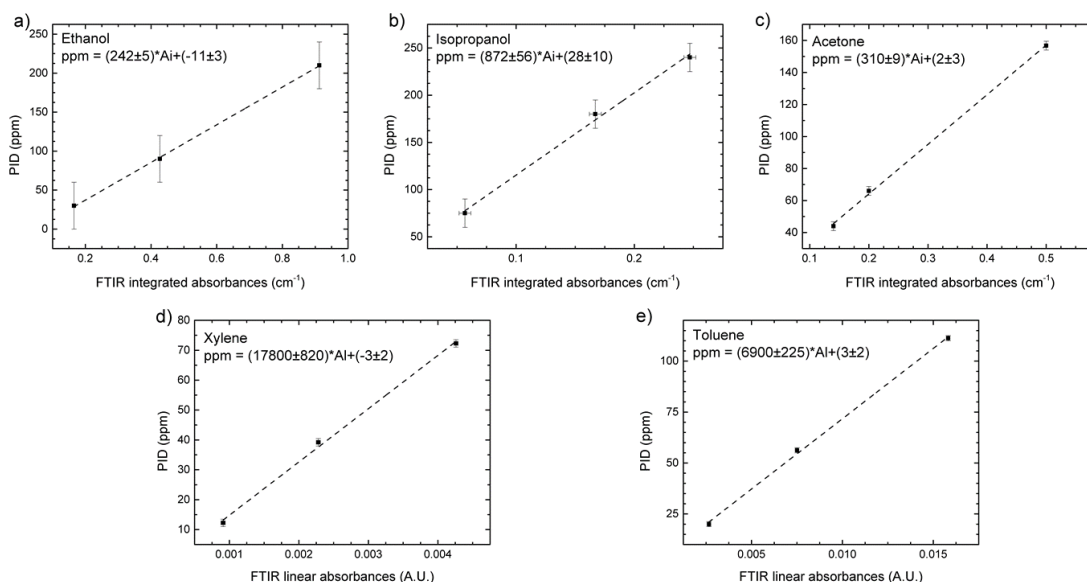


Figure 6. Calibration curves for the analyzed VOCs. Linear intensity (band height) was used for xylene and toluene. Conversion Factors for converting the PID readings in ppm

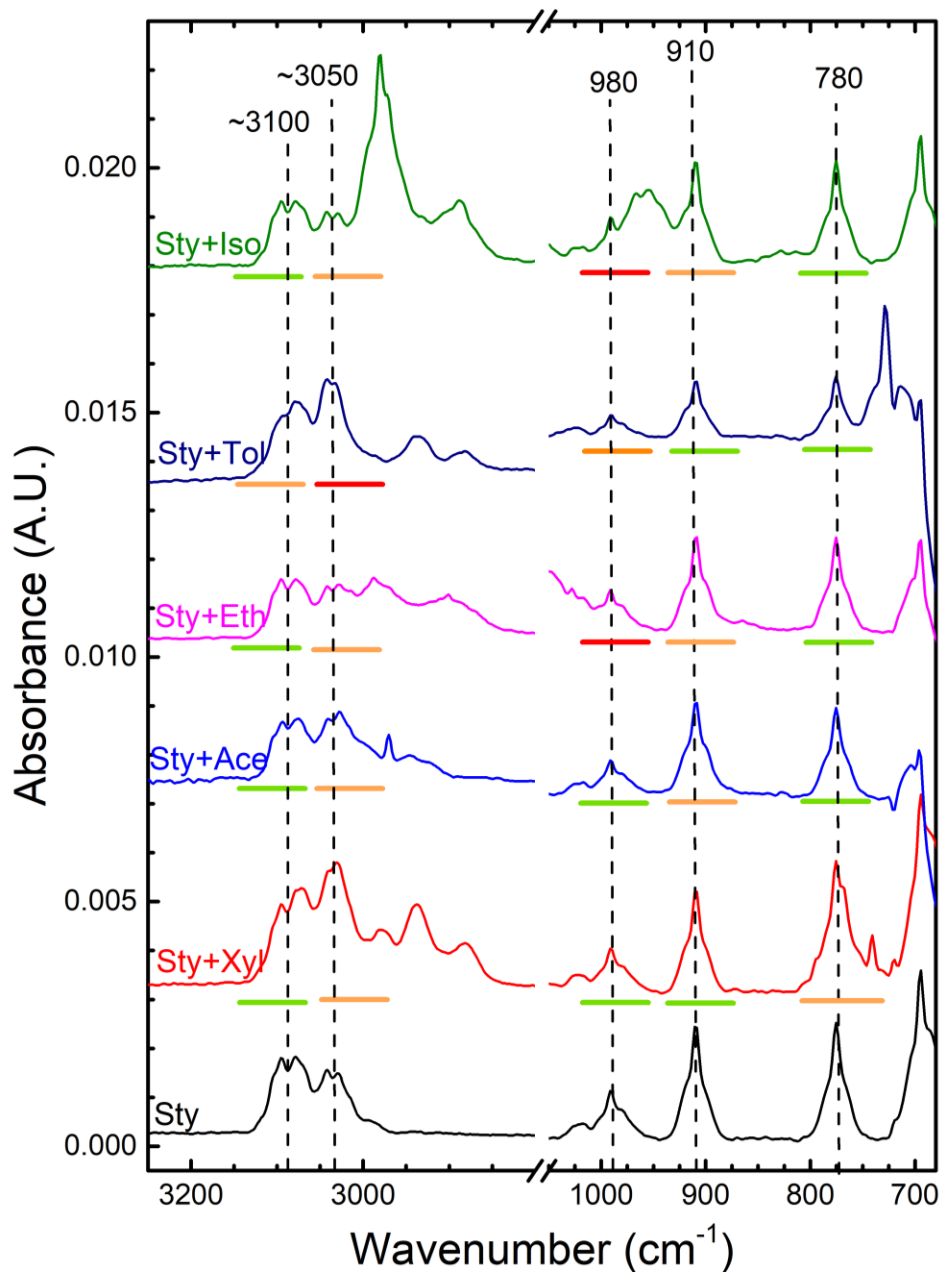
1 for all VOCs except styrene are calculated as $CF = CF_{\text{TargetVOC}}/CF_{\text{sty}}$ using the
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3 $CF_{\text{TargetVOC}}$ reported in [11] for a 10.6 eV lamp and listed below. Acetone: integration of
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5 band at 1217 cm^{-1} , CF 2.75. Ethanol: integration of band at 1066 cm^{-1} , CF 30.
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7 Isopropanol: integration of band at 954 cm^{-1} , CF 15. Xylene: integration of band at 740
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9 cm^{-1} , CF 1.225. Toluene: integration of band at 729 cm^{-1} , CF 1.25.
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16 Even with a limited number of experimental points, the data in **Figure 6** shows an
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18 excellent correlation between the absorbance of the selected band in the infrared
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20 spectrum for each substance investigated versus the PID readings for the same
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22 compound once volatilized in the sample chamber. This information, together with the
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24 data in **Figure 3** suggests that (1) different compounds can be discriminated efficiently
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26 by using the appropriate spectral region where the band overlappings are minimized; (2)
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28 there is a well-defined relationship between the gas amount in the analysed atmosphere
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30 and the integrated intensities of the reference bands in the MIR spectra, at least down to
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32 few ppm, and (3) the amount of the single volatile phase can be obtained from the MIR
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34 spectrum once the calibration curve has been established. This also implies that, when
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36 the overlap of bands is limited, the technique can be extended to the quantitative
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38 analysis of multiphase gas mixtures.
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50 *The analysis of gas mixtures*

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52 **Figure 7** shows the magnified infrared spectral region of pure styrene ($1050 - 675 \text{ cm}^{-1}$)
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54 and those of binary styrene mixtures ($3025 - 2900 \text{ cm}^{-1}$) plus a second VOC. The IR
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56 absorption bands selected for styrene are indicated by dashed lines, while the horizontal
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1 coloured segments highlight the regions where overlapping of the bands occurs. The
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3 various colours indicate the different degree of overlap: in red it is severe, in orange it is
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5 partial and in green is minor or negligible.
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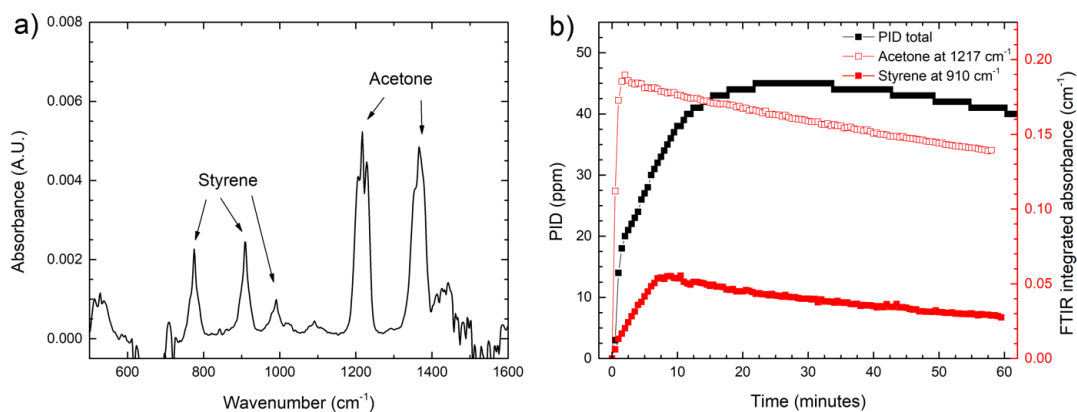


52 **Figure 7.** Examples of FTIR spectra from a mixture of styrene plus an additional VOC.

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54 The dashed lines show the position of the absorption bands (or groups of bands) of
55 interest for the analysis of styrene with respect to the other VOCs. The horizontal
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1 highlight the possible overlapping of bands: strong overlapping (in red), partial
2 overlapping (in orange) and minor to no overlapping (in green).

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9 The following example is the result of a blinded test performed to verify the possibility
10 to quantify unknown quantities of a mixture of two VOCs released into the
11 spectrophotometer chamber. For this experiment, 3 μL of styrene and 3 μL of acetone,
12 initially unknown to the researcher, were introduced into the sample compartment and
13 allowed to evaporate.
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40 **Figure 8.** (a) FTIR absorption spectrum collected for the blind test; the bands used for
41 identification are indicated by arrows. (b) Integrated FTIR absorbance trends (in red)
42 and PID readings (in black) as a function of time. Absorbance values have been
43 obtained by integrating the 910 cm^{-1} styrene band and 1217 cm^{-1} acetone band.
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53 **Figure 8a** shows the MIR spectrum of the resulting gas mixture; **Figure 8b** shows the
54 graph of the PID readings and the integrated absorbance (A_i) of the selected infrared
55 bands. The identification of the substances in the binary gas has been easily obtained by
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1 comparing the spectrum of **Figure 8a** with that of the pure substances in **Figure 3**.
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 3 Consequently, the mixture consists of styrene (bands at 780, 910 and 990 cm^{-1}) plus
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 5 acetone (bands at ~ 1217 and ~ 1370 cm^{-1}). Therefore, the bands peaking at 910 and 1217
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 7 cm^{-1} have been integrated to obtain the graphs in **Figure 8b**. The control of the
 8
 9 evolution of the integrated absorbances (**Fig. 8b**) allows differentiating the typical
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 11 behaviour of the two liquids: the evaporation of acetone is much faster than that of
 12
 13 styrene, in accordance with the different vapour pressures (0.38 vs 0.01 bar at 30°C) of
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 15 the two gases (see also **Fig. 4**). The cumulative PID curve (the PID sensor reads both
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 17 substances at the same time) shows a strong increase in the first minutes, probably
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 19 driven by the acetone faster evaporation. The maximum values of the styrene and
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 21 acetone absorbance have been plotted on the calibration curves in **Figures 5** and **6**,
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 23 respectively. The PID curve maximum, instead, has been calculated to represent the
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 25 total value (in ppm) for the gas mixture.
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 29 The final results are summarized in **Table 2**. The quantities of liquids obtained from the
 30
 31 analysis, i.e. 3.6 ± 1.4 μL of styrene and 3.3 ± 1.5 μL of acetone, agree within the error
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 33 with the quantity of liquids released into the measurement chamber at the beginning of
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 35 the experiment (both 3.0 ± 0.4 μL).
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45 **Table 2.** Blinded test results. ppm_{eq} for acetone are calculated by dividing the
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 47 concentration by acetone CF factor 2.75.
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	Styrene	Acetone
Integrated absorbance	0.0554	0.1897
(A_i)		

Dose μL (calculated)	3.6 ± 1.4	3.3 ± 1.5^a
ppm/ppm _{eq} VOC (calculated)	$27 \pm 3/\text{n.a.}$	$61 \pm 5/22 \pm 2^b$

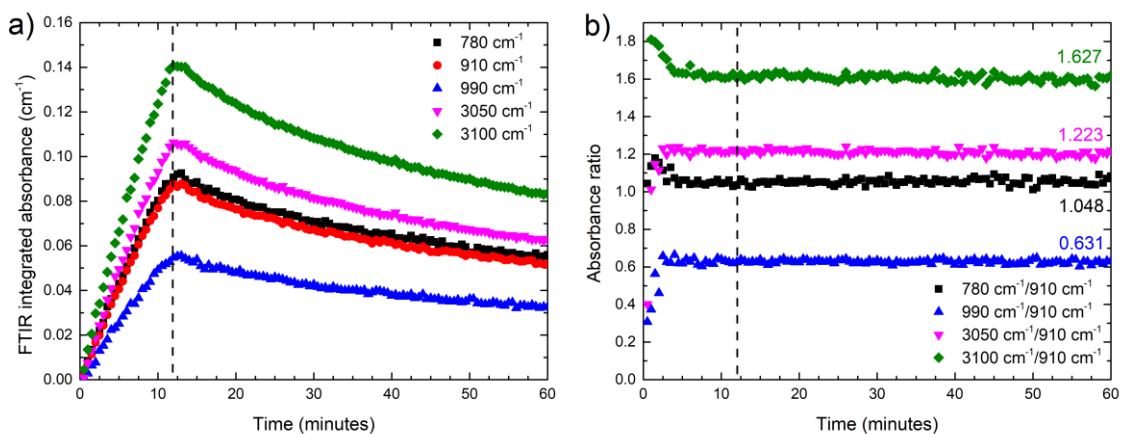
^a μL of acetone = $(15.6 \pm 2.6) \cdot A_i + (0.3 \pm 0.9)$

^bppm_{eq} of acetone = ppm/2.75, i.e. styrene to acetone Conversion Factor.

The large error associated with the prediction reflects the scatter of the data shown in **Figure 5b**. The calculated concentration for styrene and acetone is 27 ± 3 and 61 ± 5 ppm, respectively. The sum of the estimated concentration of styrene (ppm) and the equivalent concentration of acetone (ppm_{eq}) in the atmosphere inside the chamber is (49 ± 5) , which is also in excellent agreement with the total value provided by the photoionization detector (45 ± 1 ppm).

The data in **Figure 7** show that the diagnostic bands of styrene are often partially or totally overlapping those of other compounds. In the above example, we have reported a simple measurement in a mixture of styrene and acetone, which, from the spectrum given in **Figure 6** is a rather favourable case where the characteristic bands being well separated. However, considering the large amounts of possible substances present in the atmosphere of a workplace, it is clear that the presence of other gases can significantly hinder an accurate quantification of styrene. For this reason, being able to use for detection different infrared absorption bands at the same time can increase the chance of getting accurate results. The calibration provided by **Figure 5** has been performed for the 910 cm^{-1} band. However, similar calibrations can also be achieved using other signals. **Figure 9a** compares the integrated intensities of five of the main bands in the

1 MIR spectrum of styrene. The data show clearly that the trends for all vibrational modes
 2 are identical to that of the 910 cm^{-1} , showing a large increase in the first 12 minutes,
 3 similar maxima and a smooth decrease. The same trend is observed using the band ratio
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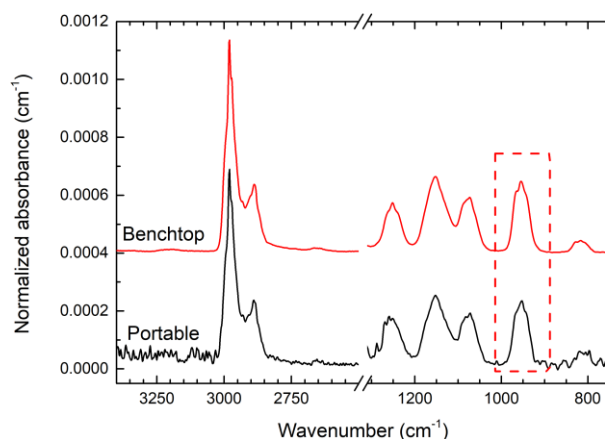


51 **Figure 9.** (a) Integrated FTIR absorbance trends with time for selected styrene bands
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Toward a compact and portable device

After validation and calibration of the technique with styrene, we performed the experiments with a portable FTIR spectrometer (**Fig. 2**) with the main purpose of testing the reproducibility of the methodology with a compact, handy and portable device. The rationale behind this research was the design of a sensing system suitable for work sites that require monitoring of VOCs in the atmosphere. For these tests we used ethanol, acetone and isopropanol as proxies to verify the reliability of the set up and the method.

Figure 10 shows the MIR spectrum of isopropanol collected with both the compact



device (black) and the benchtop set-up (red) for the same gas concentration (~240 ppm).

Figure 10. FTIR spectra of the same amount of isopropanol (~240 ppm) in the atmosphere collected with either the portable spectrometer (black line) or the benchtop spectrometer (red lines). Spectra are normalized to the beam path (Eq. 1). The band used for calibration is highlighted in the box.

As expected, the spectra are identical, particularly for the bands used for the calibrations (highlighted in the box). Therefore, for these concentrations, using the main absorption bands, both instruments allow collecting data with similar resolution. The data in **Figure 10** show, however, that the portable device does not allow resolving the less intense bands (see for example the 818 cm^{-1} band) with sufficient S/N (signal-to-noise) ratio for an accurate quantification. This also implies that very low concentrations levels (ppb) cannot be detected with the short sampling path of the portable gas cell (7 cm vs. 25.5 cm of the benchtop instrument).

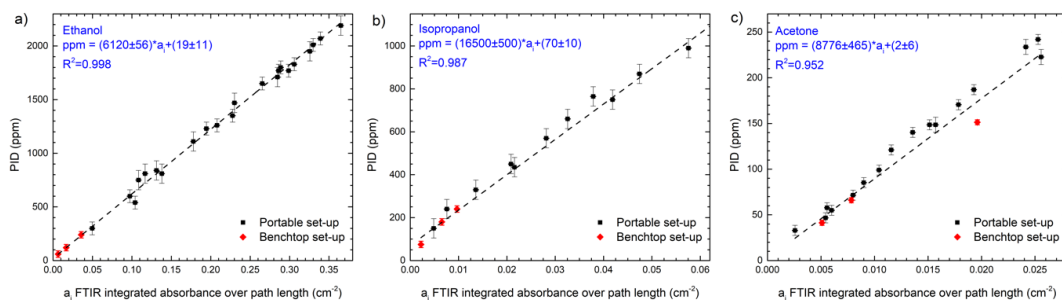


Figure 11. Calibration curves for ethanol (a), isopropanol (b) and acetone (c). Red diamonds: benchtop; black squares: portable spectrometer. Absorbances are scaled to the FTIR path length.

Figure 11 shows the calibration curve obtained for ethanol, isopropanol and acetone by combining the data from the benchtop and the portable spectrometer. For all the gases examined, the data obtained with the portable device are in agreement with those of the benchtop instruments. Ethanol and isopropanol, however, showed a slightly better correlation than acetone (**Fig. 11c**). In **Figure 11** the data obtained using the two different layouts have been normalized to the sampling path length (a_i) (7 cm for the

1 portable and 25.5 cm for the benchtop spectrophotometer). These graphs, therefore,
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3 confirm that both configurations can be successfully used for quantitative gas
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5 concentration measurements.
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10 **Conclusions**

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12 Real-time analysis of toxic volatile organic compounds in closed environments
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14 represents a challenge in environmental monitoring, particularly in discriminating
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16 between different substances with a high accuracy level. Optical techniques are
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18 extremely valuable in this regard, and several tests have been carried out to use them for
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20 in situ applications. An example is a system capable of detecting and quantifying
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22 several VOCs in the sub-parts per million range which has been installed in a Waste
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24 Isolation Pilot Plant at Carlsbad (New Mexico, USA) [10]. An excellent detection
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26 resolution on various VOCs present in the site, both as normal constituents of ambient
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28 air or as a by-product of industrial activities, has been reported. However, the
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30 instrumentation, which is based on multi-pass optical cells to improve the detection
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32 limit, can only be used as a fixed installation [14]. Specific software can improve
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34 handling the data obtained in open-path FTIR measurements. This advanced method has
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36 been applied to field measurements done using a light source and a retroreflector placed
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38 in the open air in Seoul (Korea) Olympic Park, at a distance of 144 m from each other.
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40 High detection rates for a broad spectrum of airborne chemical species, using non-
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42 portable instrumentation, have been achieved.
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52 In the present work, we have studied the possibility of scaling down the infrared
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54 instrumentation toward truly portable and miniaturized spectrometers for real time
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56 monitoring of VOCs in working places. We have calibrated the system for styrene and a
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1 series of VOCs of environmental interest and demonstrated that the technique allows
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3 discriminating between different gaseous compounds in the atmosphere to get very
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5 accurate quantitative information on their concentration. The method is effective also
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7 when different VOCs are present in a gas mixture.
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10 The feasibility of FTIR detection methods to implement portable instrumentation for
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12 indoor monitoring of styrene and associated VOCs in working sites has been exploited.
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14 To this purpose, we have used in our experiments a commercial compact and fully
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16 portable instrument obtaining a resolution comparable to the laboratory equipment. The
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18 proposed technology, therefore, appears extremely promising to build improved mobile
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20 sensors to detect potentially toxic VOCs in indoor environments. Increasing the
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22 instrument miniaturization may imply some drawbacks to face such as an enhanced
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24 background noise that could affect the detection of weak signals in multi-phase spectra.
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26 There are several possibilities to handle this problem, for instance, improving the data
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28 analysis and treatment. Some examples are the characteristic wavelength selection via
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30 Monte-Carlo sampling [15] or the use of machine-learning algorithms [16] coupled with
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32 a gas-phase database, or partial least square multivariate calibrations [17]. These data
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34 analysis methods have already been tested [18] for quantitative measurements of
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36 volatile organic compounds. Their integration in portable systems for the real-time
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38 detection in workplaces is the next challenge to face.
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- *Graphical Abstract (for review)*
- *Manuscript*
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Dear Editor,

the following reseachers come to mind as people capable of providing a thorough review of our work:

- Dr. Gianfelice Cinque (expert in infrared spectroscopy)

Principal Beamline Scientist for the Multimode InfraRed Microscopy And Imaging (MIRIAM) beamline

Diamond Light Source, Oxfordshire, UK

Email: gianfelice.cinque@diamond.ac

- Dr. Ulrich Shade (expert in real-time infrared spectroscopy)

Photon Science division

Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany

Email: ulrich.schade@helmholtz-berlin.de

- Dr. Lisa Vaccari (expert in infrared spectroscopy)

SISSI - Synchrotron Infrared Source for Spectroscopy and Imaging

Elettra Synchrotron Light Laboratory, Trieste, Italy

Email: lisa.vaccari@elettra.eu

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: